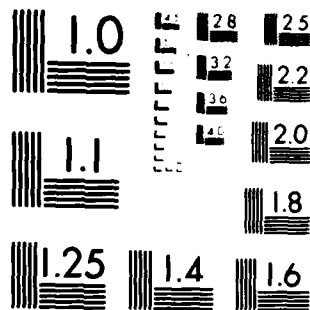END

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Ultrasonic Relaxation spectra of the systems $LiAsF_6$ added to the macrocycles 18C6 or 12C4 ethers, in molar ratio $R \approx 1$, in the solvent 1,2-Dimethoxyethane (DME) at t=25°C are reported. The concentration range covered was 0.05 to 0.25M for 18C6 and 0.1 to

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Abstract  Continued:

$\sim$0.3M for 12C4.  Ancillary electrical conductance data for the same systems in the concentration range $10^{-4}$ to $\sim$ 0.05M at 25.00 C reveal that the lithium-macrocycle interaction is weak, the conductance data being the same up to $\sim 10^{-2}$M, within experimental error of the one for the electrolyte in DME.

Based on a previous work revealing the presence of an outer sphere-inner sphere equilibrium $LiSAsF_6 \rightleftharpoons LiAsF_6$ the present data are interpreted by a mechanism envisaging competition between the above reaction and the complexation scheme $LiSAsF_6 + C \rightleftharpoons LiC,AsF_6 + S$ where C is the crown ether.  The results for $LiAsF_6$ + 18C6 are compared with previous one for the system $LiClO_4$ + 18C6 in DME.

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"KINETICS OF COMPLEXATION OF THE MACROCYCLES

18C6 AND 12C4 ETHERS WITH $LiAsF_6$ in 1,2-

DIMETHOXYETHANE AT 25°C".

TECHNICAL REPORT #5

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# KINETICS OF COMPLEXATION OF THE MACROCYCLES 18C6 AND 12C4 ETHERS WITH LiAsF$_6$ IN 1,2-DIMETHOXYETHANE AT 25°C

By

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## Abstract

Ultrasonic Relaxation spectra of the systems LiAsF6
added to the macrocycles 18C6 or 12C4 ethers, in molar ratio
R≈1, in the solvent 1,2-Dimethoxyethane (DME) at t=25°C are
reported. The concentration range covered was 0.05 to 0.25M
for 18C6 and 0.1 to 0.3M for 12C4. Ancillary electrical con-
ductance data for the same systems in the concentration range
$10^{-4}$ to ~0.05M at 25.00°C reveal that the lithium-macrocycle
interaction is weak, the conductance data being the same up to
~$10^{-2}$M, within experimental error of the one for the electrolyte
in DME. Based on a previous work revealing the presence of an
outer sphere-inner sphere equilibrium LiSAsF6⇌LiAsF6, the pre-
sent data are interpreted by a mechanism envisaging competition
between the above reaction and the complexation scheme LiSAsF$_6$
+C⇌LiC,AsF$_6$+S where C is the crown ether. The results for
LiAsF$_6$ + 18C6 are compared with previous one for the system
LiCℓO$_4$ + 18C6 in DME.

## I. Introduction

In previous works[1,2] it has been found that $LiAsF_6$ in the solvent 1,2-DME is the strongest electrolyte system so far investigated, which, in principle, could be used for construction of secondary lithium batteries. It was of interest to see whether one could further enhance the electrical conductivity of this system by adding complexing agents to $Li^+$ as crown-ethers. It was also of interest to determine the rate constants of formation and dissociation of the crown ether with the cation, as a too stable complex is unsuitable for the electrochemical reactions at the electrode surface.

These practical interests went alongside more theoretical quests as the extent of interaction of crown-ethers with a cation already solvated by DME which (by structure and chelating ability) mimics a part of a crown ether. As $LiClO_4 + 18C6$ in DME had already[3] been investigated, a comparison with $LiAsF_6 + 18C6$ in DME would offer an insight into the role (if any) of the anion in the complexation mechanism. This research in a strongly competing solvent, for the first coordination around $Li^+$, will be the prelude and background of future work in solvents of less competitive nature, but more in use for battery construction.

To the above end, two experimental methods, audiofrequency electrical conductivity in the electrolyte concentration $10^{-4}$ to $5 \times 10^{-2} M$, and ultrasonic relaxation spectrometry in the frequency range 1-400 MHz and electrolyte concentration range 0.05-0.3M have been used.

## II. Experimental

The equipment and procedure for the conductance[4] and ultrasonic work[2] have been described elsewhere. For the materials $LiAsF_6$,[1] 1,2-DME[3] and 18C6[3] were purified as already reported. 12C4 (Aldrich) was vacuum distilled. Solutions were prepared by weight burettes directly in the conductance cell, kept at $t = 25.00 \pm 5 \times 10^{-3}$ as monitored by a calibrated Pt-thermometer and Mueller bridge.[4] The conductance room was air-conditioned at $71 \pm 1 °F$. For the ultrasonic work, solutions were prepared in volumetric flasks, kept in dessicators and used shortly after preparation. Contact of the solutions with the atmosphere was kept to a maximum of 20-30 seconds during the filling time of the cells.

## III.  Results

Fig. la reports the equivalent conductance vs. concentration in the form of $log_{10} \Lambda$ vs. $log_{10}C$ for $LiAsF_6 + 18C6$ in molar ratio $R = [\ 18C6]/[\ LiAsF_6] = 0.958$ at $25^{\circ}C$. In the same plot the data for $LiAsF_6$ in DME[1] are also reported. The two sets of data overlap within experimental error, indicating a weak or non detectable interaction between $LiAsF_6$ and 18C6.

Fig. lb reports the equivalent conductance vs. concentration ($log_{10} \Lambda$ vs. $log_{10}C$) for $LiAsF_6 + 12C4$ in DME at $25^{\circ}C$. Two runs at molar ratios $R = 0.974$ and $R = 1.004$ have been performed. As for the case of 18C6, no difference, within experimental error, is visible from the data of the electrolyte $LiAsF_6$ in DME except for $c > 10^{-2}M$. This again indicates weak interaction between $Li^+$ and 12C4 in DME, a vital information for the interpretation of the ultrasonic data. Notice that $LiClO_4 + 18C6$ in DME shows the same behavior in conductance,[5] except for data at $c \geq 10^{-2}M$ where a difference starts showing up when the crown ether is present.

Fig. 2 reports the ultrasonic spectrum vs. frequency f in the form of the excess sound absorption per wavelength $\mu$ for a representative concentration of $LiAsF_6$ added to 18C6 in DME at $25^{\circ}C$. In the above $\mu = (\alpha - Bf^2)u/f$, where $\alpha$ is the absorption coefficient of sound (neper $cm^{-1}$) at the frequency f; B is the background sound absorption, $\alpha$ at $f \gg$ (the relaxation frequencies) $f_I$ and $f_{II}$ (see below), u/f is the wavelength, u is the sound velocity. The solid line in Fig. 2 is the calculated sum of two Debye single relaxation processes used to interpret the spectrum

$$\mu = 2\mu_I \frac{f/f_I}{1 + (f/f_I)^2} + 2\mu_{II} \frac{f/f_{II}}{1 + (f/f_{II})^2} \qquad (1)$$

where $f_I$ and $f_{II}$ are the relaxation frequencies of the two Debye processes. $\mu_I$ and $\mu_{II}$ are the respective maximum sound absorptions per wavelength. It should be pointed out that other mathematical solutions for the interpretation of the sound spectrum may be possible including a distribution of relaxation times. The present one is the simplest possible interpretation of the spectrum. Fig. 3 shows a representative plot of the ultrasonic spectrum vs. frequency f, in the form of $\mu$, for a representative concentration of

LiAsF$_6$ added to 12C4 in DME at 25$^{\circ}$C. The solid line in Fig. 3 is the calculated sum of two Debye relaxation processes of excess maximum sound absorption per wavelength $\mu_I$ and $\mu_{II}$ centered at the relaxation frequencies f$_I$ and f$_{II}$.

Table I reports all the calculated ultrasonic relaxation parameters together with the sound velocity u at the concentrations investigated in DME at 25$^{\circ}$C.
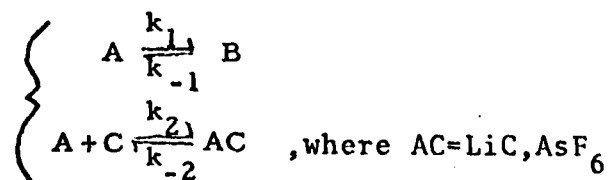
IV. Discussion

In a previous work the ultrasonic relaxation of LiAsF$_6$[1] was attributed to the equilibrium

$$\text{LiS, AsF}_6 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{LiAsF}_6 + \text{S} \qquad (2)$$
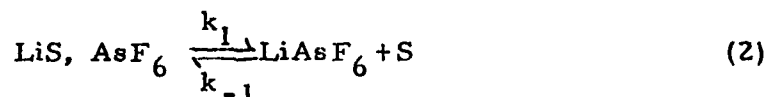
when S is a solvent molecule. The above scheme (2) symbolizes an outer-sphere, inner-sphere equilibrium. Electrical conductance for both macro-cycles 18C6 and 12C4 suggests that their interaction with Li$^+$ is weak in DME. We then propose that there exists a competition between scheme (2) and the complexation reaction

$$\text{LiS, AsF}_6 + \text{C} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \text{LiC, AsF}_6 + \text{S} \qquad (3)$$
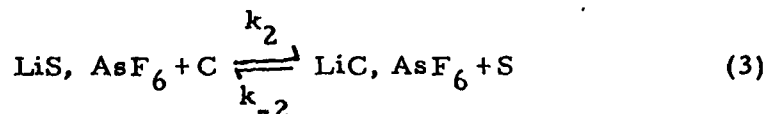
with C, the macrocyle. Call LiS, AsF$_6$ = A; LiAsF$_6$ = B. One can combine schemes 2 and 3 (omitting S, in excess), to:

$$\left\{ \begin{array}{l} \text{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{B} \\[2ex] \text{A} + \text{C} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \text{AC} \quad , \text{where AC=LiC,AsF}_6 \end{array} \right.$$

and write the rate equations

$$\left\{ \begin{array}{l} -\dfrac{d(A)}{dt} = k_1(A) - k_{-1}(B) + k_2(A)(C) - k_{-2}(AC) \\[3ex] \dfrac{d(AC)}{dt} = k_2(A)(C) - k_{-2}(AC) \end{array} \right. \qquad (4)$$

leading to(see Appendix) two relaxation times $\tau_I$ and $\tau_{II}$

$$\tau_I^{-1} = \tfrac{1}{2}\left[ S + \sqrt{S^2-4P}\right]; \quad \tau_{II}^{-1} = \tfrac{1}{2}\left[ S - \sqrt{S^2-4P}\right]$$

with $S = k_2\{(A) + (C)\} + k_{-2} + k_1 + k_{-1}$

and $P = (k_1+k_{-1})\left[k_2(A)+k_{-2}\right] + k_2 k_{-1}(C)$

for $\tau_I^{-1}(=2\pi f_I) \gg \tau_{II}^{-1}(=2\pi f_{II})$ as it is the case for the present

work $S^2 \gg 4P$ and $\tau_I^{-1} = S = k_2\{(A)+(C)\} + k_{-2} + k_1 + k_{-1} \approx k_1 + k_{-1}$     (5)

$$\tau_{II}^{-1} = \frac{P}{S} = k_{-2} + k_2\left[(A) + \frac{k_{-1}}{k_{-1}+k_1}(C)\right] \tag{6}$$

From the study of the electrolyte $LiAsF_6$ alone in DME,[1] we have

learned that for equilibrium (2) $K_1 = \dfrac{(LiAsF_6)}{(LiSAsF_6)} \approx 10^{-2}$. Hence since

$K_1 = k_1/k_{-1}$, $k_1 \ll k_{-1}$ and equation (6) becomes $\tau_{II}^{-1} = k_{-2} + k_2\left[(A)+(C)\right]$   (7)

which implies that the coupling factor $(k_{-1}/(k_1+k_{-1}) \approx 1$.

Equation 7 will be tested for $LiAsF_6$ + 18C6 and $LiAsF_6$+12C4 in DME

assuming $(A) \approx C_{LiAsF_6}$ and $(C) \approx C_{18C6}$ or $\approx C_{12C4}$ by virtue of the

suggested weak interaction between crown ethers and metal cations

from conductance data.

Fig. 4 shows the plots of $\tau^{-1}$ vs. $(C_{LiAsF_6} + C_{Macrocycle})$. For 18C6

linear regressions give determination coefficient $r^2 = 0.99$, Inter-

cept$= k_{-2} = 1.6\times10^7$ $S^{-1}$, Slope$= k_2 = 1.4\times10^8$ $M^{-1}$, from which $K_2 = 8.8 M^{-1}$.

For 12C4, linear regressions give $r^2 = 0.7$, Intercept$= k_{-2} = 5.5\times10^6$ $S^{-1}$,

Slope$= k_2 = 1.9\times10^7$ $M^{-1}$ $S^{-1}$ from which $K_2 = 3.5 M^{-1}$.

Notice that for $LiClO_4 + 18C6$ in DME[3] plotting $\tau_2^{-1}$ vs. $(C_{LiClO_4} + C_{18C6})$, namely neglecting the coupling with the dimerization $2LiClO_4 \rightleftharpoons (LiClO_4)_2$[3,6], one obtains[3] $r^2 = 0.999$ $k_{-2} = 6.6 \times 10^6 S^{-1}$, $k_2 = 2.4 \times 10^8 M^{-1} S^{-1}$ namely a forward rate constant within a factor of two for the two electrolytes reacting with 18C6 in DME. Speculations about the differences in $k_2$ and $k_{-2}$ are negated by the numerical approximations made in relation to the respective coupled reactions for the two systems.

It is interesting to notice that the macrocycle 12C4 seems to react a factor of ten slower than 18C6 with $LiAsF_6$ in DME. The two macrocycles differ by the size of the cavity and their rigidity, 12C4 almost matching the $Li^+$ cation radius. The reasons for 12C4 reacting slower than 18C6 may be invoked from more rigidity of the ligand 12C4 and from the possible requirement of complete desolvation of $Li^+$ when reacting with 12C4. Without further structural information, these reasons as well as possible alternate ones, remain clearly speculative rationalizations of an experimental observation.

## Conclusion

For the present solvent system, the weak interaction of both macrocycles with $Li^+$ has been established, as well as the relative lability of the complexes formed. The practical goals envisaged by the use of crown ethers in the introduction, do not seem feasible in DME. This solvent chelates the cation and by overwhelming mass effect competes effectively with the macrocycles. The situation may become \dramatically different in other solvents where ionization of the electrolyte is an urgent practical requirement. Work is now planned along these lines.

## References

\* On leave from the Max-Planck Institute for biophysical chemistry, Goettingen-Nikolausberg, Germany W.

\*\*On sabbatical leave from Fukui University, Fukui, Japan

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6) Onishi S., Farber H., Petrucci S., J. Phys. Chem. (1980), 84, 2922

## TABLE I

Ultrasonic relaxation parameters * $\mu_I$, $f_I$, $\mu_{II}$, $f_{II}$, B and sound velocity u for $LiAsF_6$ + 18C6 and $LiAsF_6$ + 12C4 in DME at $25^\circ$ C, for the concentrations investigated.

### LiAs $F_6$ + 18C6

| $C_{LiAsF_6}$ (M) | $C_{18C6}$ (M) | $\mu_I$ x$10^5$ | $f_I$ (MHz) | $\mu_{II}$ x$10^5$ | $f_{II}$ (MHz) | Bx$10^{17}$ (cm$^{-1}$ S$^2$) | Ux$10^{-5}$ (cmS$^1$) |
|---|---|---|---|---|---|---|---|
| 0.25 | 0.25 | 500 | 100 | 400 | 14 | 48 | 1.195 |
| 0.25 | 0.25 | 600 | 110 | 460 | 14 | 48 | 1.195 |
| 0.20 | 0.20 | 450 | 110 | 400 | 11 | 48 | 1.194 |
| 0.15 | 0.15 | 500 | 80 | 360 | 10 | 42 | 1.190 |
| 0.10 | 0.10 | 320 | 90 | 280 | 7 | 40 | 1.190 |
| 0.054 | 0.055 | 270 | 80 | 300 | 5 | 36 | 1.186 |

### LiAs $F_6$ + 12C4

| $C_{LiAsF_6}$ (M) | $C_{18C6}$ (M) | $\mu_I$ x$10^5$ | $f_I$ (MHz) | $\mu_{II}$ x$10^5$ | $f_{II}$ (MHz) | Bx$10^{17}$ (cm$^{-1}$ S$^2$) | Ux$10^{-5}$ (cmS$^1$) |
|---|---|---|---|---|---|---|---|
| 0.30 | 0.29 | 550 | 100 | 140 | 3 | 50 | 1.200 |
| 0.25 | 0.25 | 570 | 85 | 100 | 2 | 49 | 1.190 |
| 0.20 | 0.20 | 450 | 80 | 80 | 2 | 48 | 1.196 |
| 0.175 | 0.175 | 370 | 90 | 85 | 1.7 | 44 | 1.180 |
| 0.10 | 0.10 | 220 | 90 | 70 | 1.7 | 42 | 1.174 |

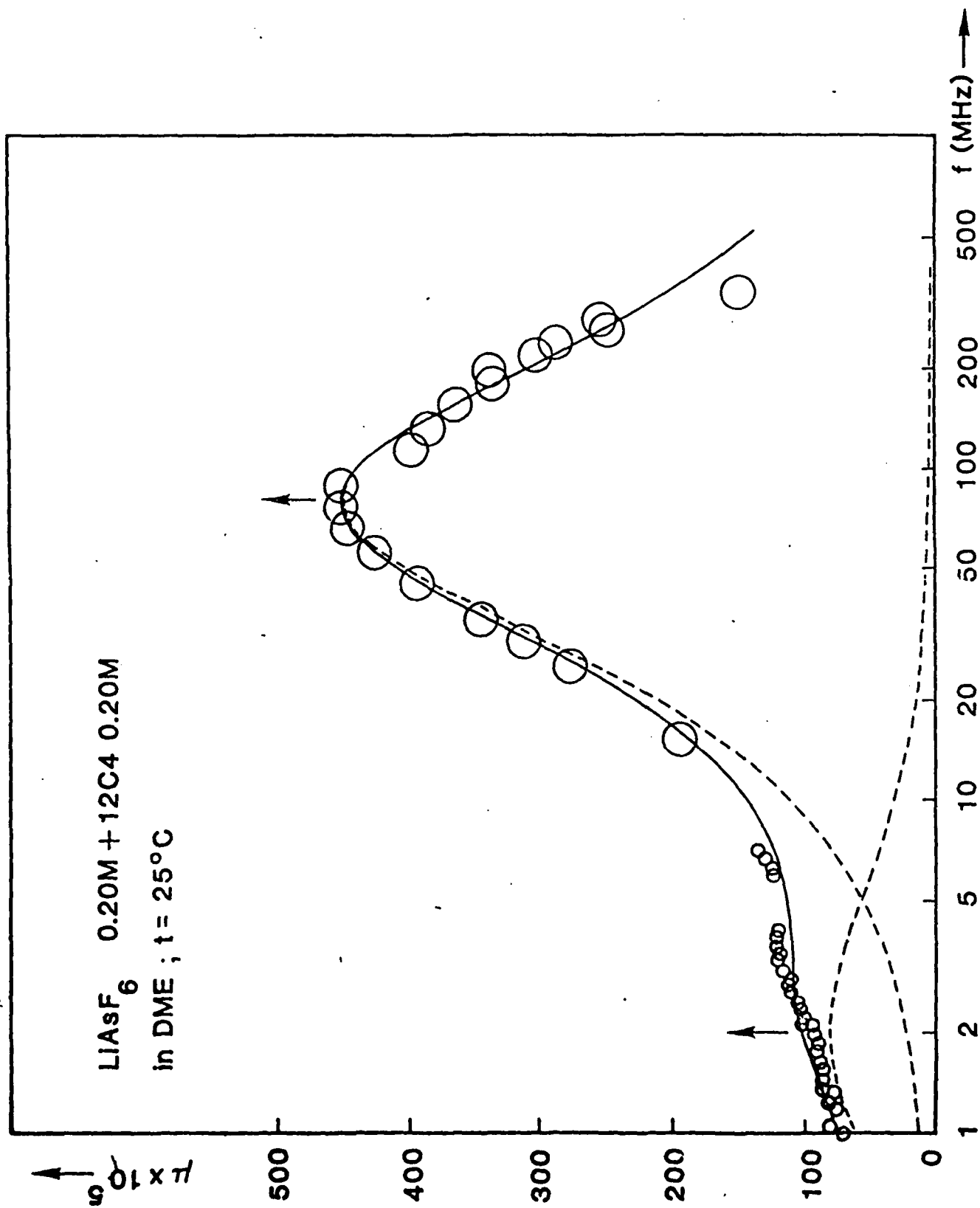* The calculated relaxation parameters are affected by an average error of $\pm 5\%$, except the parameter B which carries an error of $\pm$ 1x$10^{-17}$ (cm$^{-1}$ S$^2$). The sound velocity u is measured with an average error of $\pm 2\%$.
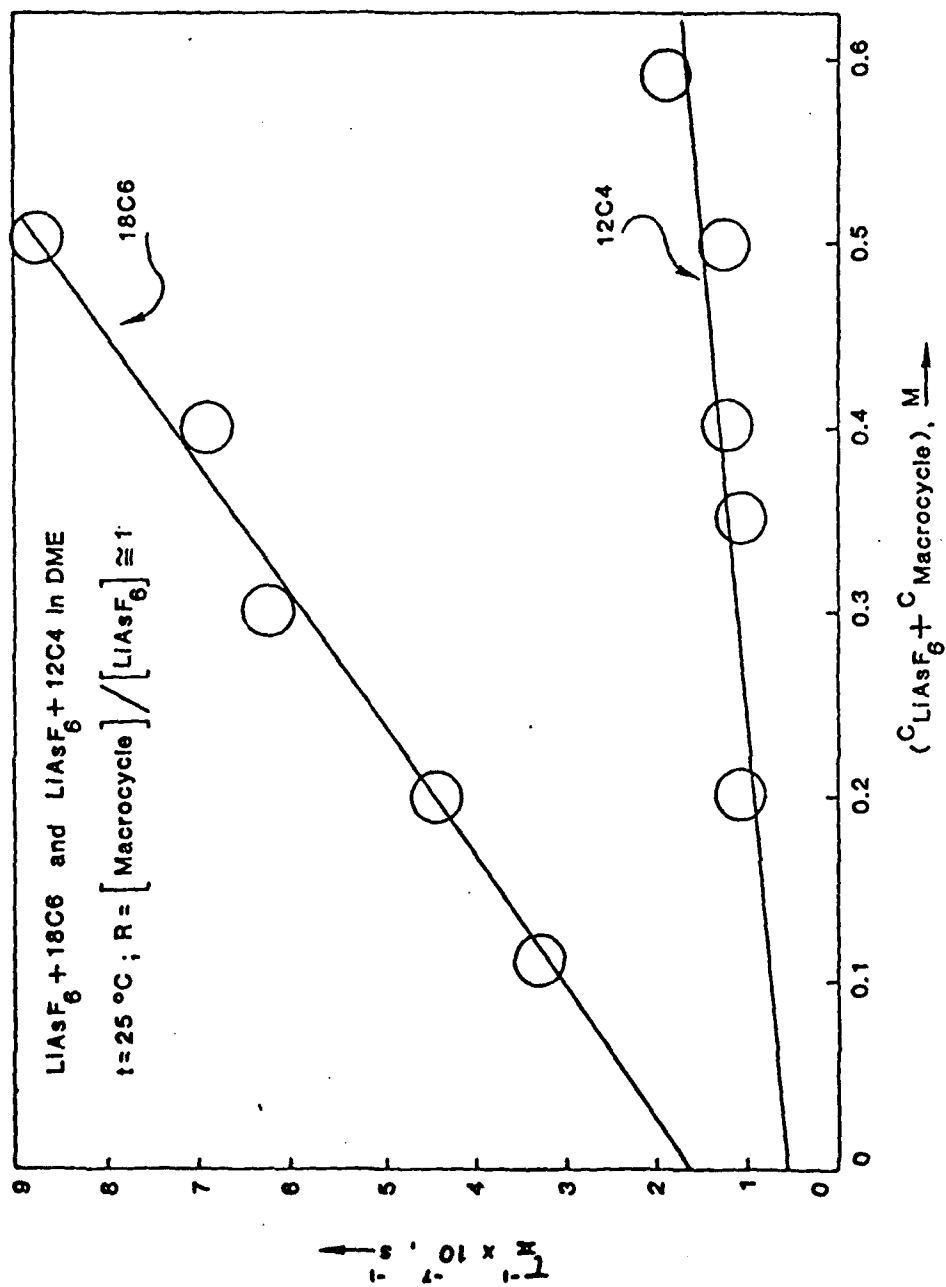
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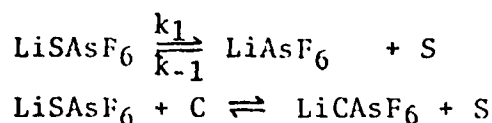
Fig. 1    A      $\log_{10} A$ <u>vs</u> $\log_{10} C$ for $LiAsF_6$ + 18C6 in DME; $t = 25^{\circ}$ C. The triangles refer to $LiAs\ F_6$ in DME (Reference 1).

Fig. 1    B      $\log_{10} A$ <u>vs</u> $\log_{10} C$ for $LiAsF_6$ + 12C4 in DME; $t = 25^{\circ}$ C. The triangles refer to $LiAsF_6$ in DME (Reference 1).

Fig. 2      Excess sound absorption per wavelength $\mu$ <u>vs</u> frequency f for $LiAsF_6$ 0.20M + 18C6 0.20M in DME; $t = 25^{\circ}$ C.

Fig. 3      $\mu$ <u>vs</u> f for $LiAsF_6$ 0.20M + 12C4 0.20M in DME; $t = 25^{\circ}$ C.

Fig. 4      $\tau_{II}^{-1}$ <u>vs</u> $(C_{LiAsF_6} + C_{Macrocycle})$ for $LiAsF_6$ + 18C6 and $LiAsF_6$ + 12C4 in DME; $t = 25^{\circ}$ C.

$\log_{10} \Lambda$ VS $\log_{10} c$ for $LiAsF_6 + 18C6$
In DME ; $t = 25.00°C$
○ $LiAsF_6 + 18C6$ ; $R = \dfrac{[18C6]}{[LiAsF_6]} = 0.958$
△,▲ $LiAsF_6$ In DME

$\log_{10} \Lambda$ VS $\log_{10} c$ for $LiAsF_6 + 12C4$
In DME ; $t = 25.00°C$
$LiAsF_6 + 12C4$ $\begin{cases} ○ R = \dfrac{[12C4]}{[LiAsF_6]} = 0.9737 \\ ● R = 1.0039 \end{cases}$
△,▲ $LiAsF_6$ In DME

LiAsF$_6$  0.20M+18C6  0.20M

in DME ; t=25°C

$\mu \times 10^6$

f (MHz)

LiAsF$_6$ 0.20M + 12C4 0.20M
in DME ; t = 25°C

LiAsF$_6$ +18C6 and LiAsF$_6$ +12C4 in DME

t=25 °C ; R = [Macrocycle]/[LiAsF$_6$] ≅ 1

18C6

12C4

($c_{LiAsF_6}$ + $c_{Macrocycle}$), M

$\tau^{-1}$ × 10$^{-7}$, s$^{-1}$

Appendix

$$LiSAsF_6 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} LiAsF_6 + S$$
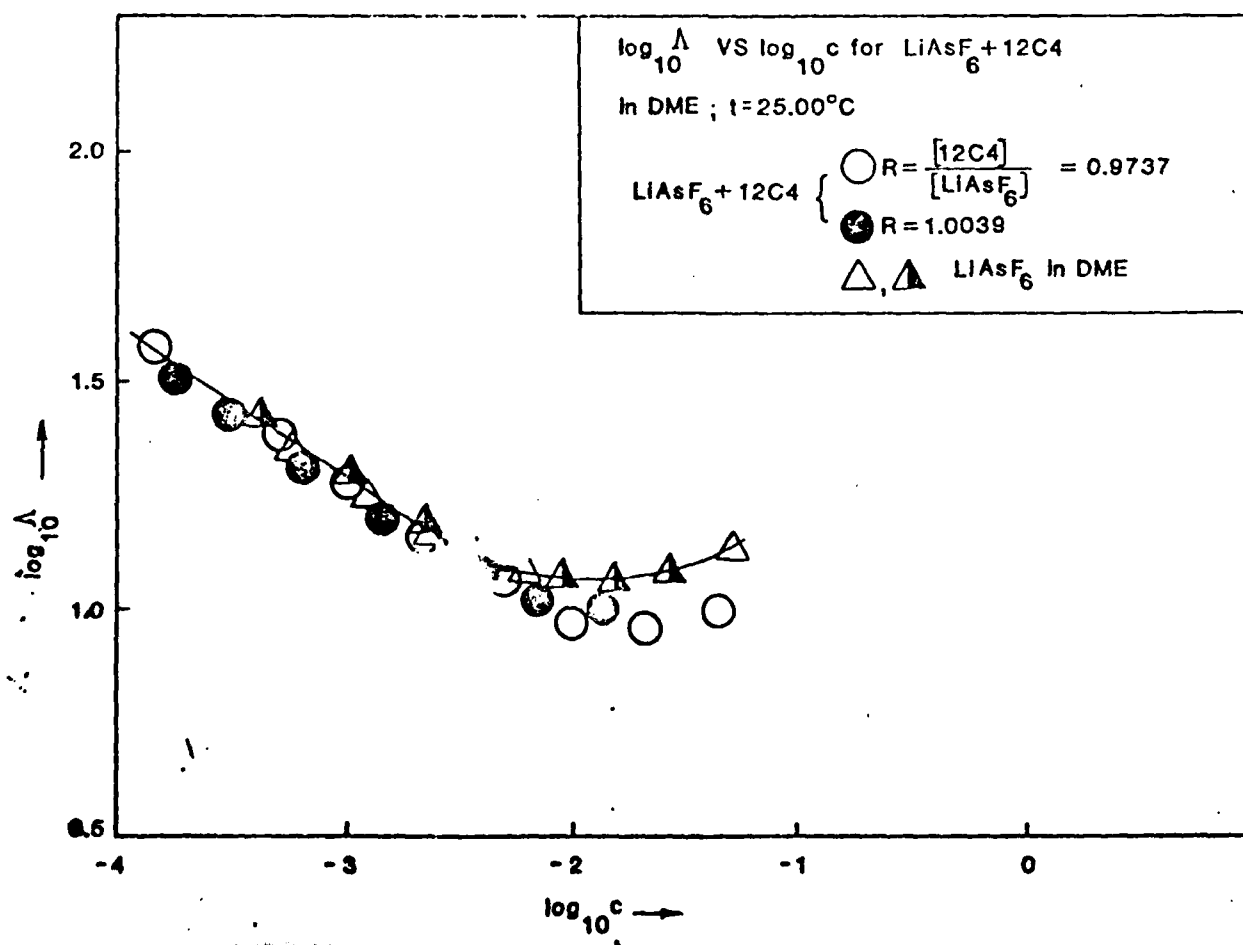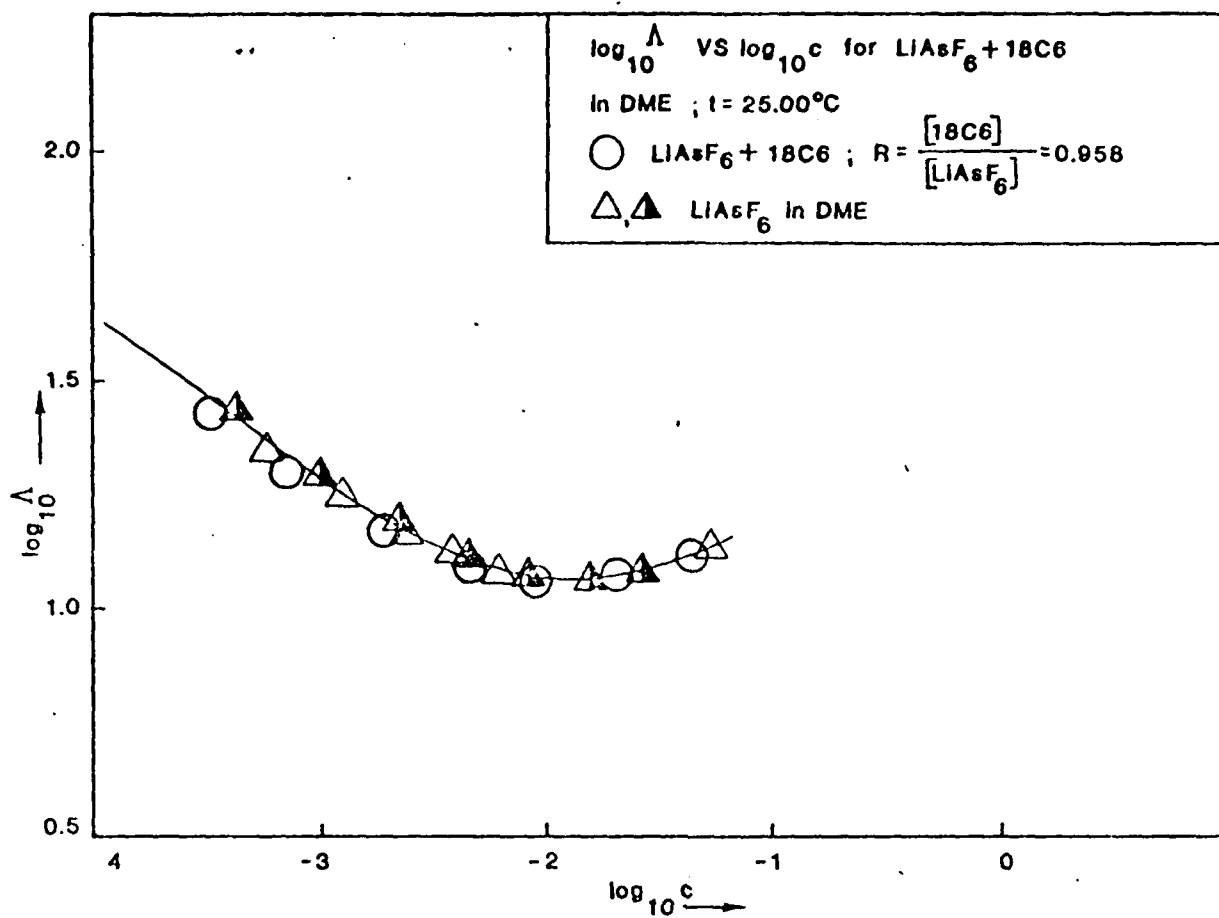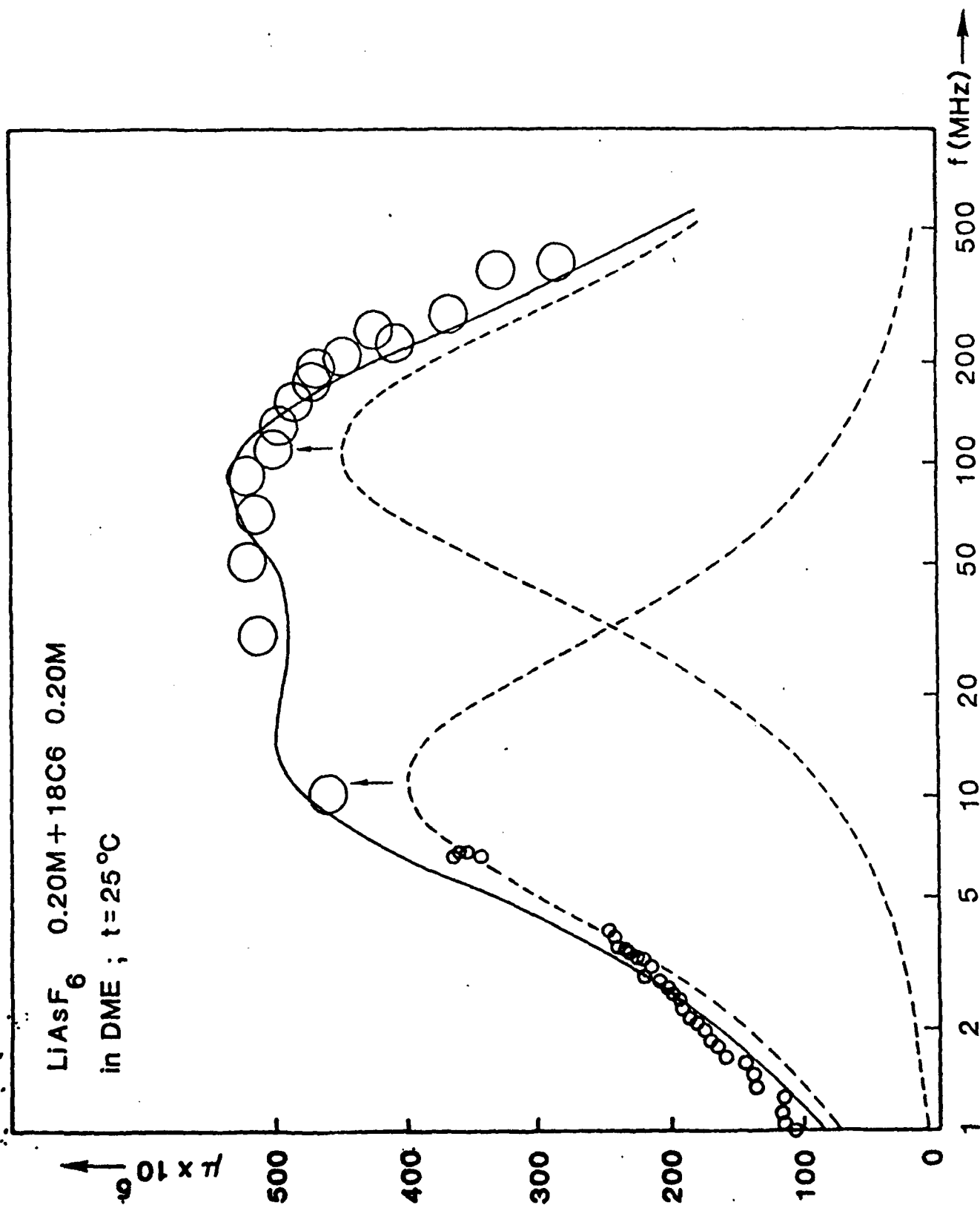
$$LiSAsF_6 + C \rightleftharpoons LiCAsF_6 + S$$

Call: $LiSAsF_6 = A$, $LiAsF_6 = B$, Omit S as the solvent is in excess.
Then:

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B$$

$$A + C \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} AC \quad \text{where, } (AC = LiCAsF_6)$$

Rate equations:

$$\frac{-d(A)}{dt} = k_1 (A) - k_{-1} (B) + k_2(A)(C) - k_2 (AC)$$

$$\frac{d(AC)}{dt} = k_2 (A) (C) - k_{-2} (AC)$$

Linearization of the rate equations gives:

$$\frac{-d\,\delta(A)}{dr} = k_1 \delta(A) - k_{-1} \delta(B) + k_2(A) \delta(C) + k_2(C) \delta A - k_{-2} \delta(AC)$$

$$\frac{d\delta(AC)}{dt} = k_2(A)\delta(C) + k_2(C)\delta(A) - k_{-2}\delta(AC)$$

From mass conservation one writes:

$(Ao) = (A) + (B) + (AC)$
$0 = \delta(A) + \delta(B) + \delta(AC)$ and $\delta(B) = -\delta(A) - \delta(AC)$
$(Co) = (C) + (AC)$
$0 = \delta(C) + \delta(AC)$ and $\delta(C) = -\delta(AC)$

Substituting, one obtains relations in $\delta(A)$ and $\delta(AC)$:

$$\frac{-d\delta(A)}{dt} = \left[k_1 + k_{-1} + k_2(C)\right]\delta(A) + \left[k_{-1} - k_2(A) - k_{-2}\right]\delta(AC)$$

$$\frac{d\delta(AC)}{dt} = k_2(C)\delta(A) - \left[k_2(A) + k_{-2}\right]\delta(AC)$$

Call $\delta(A) = \delta(Ao) e^{-\lambda t}$, $\delta(AC) = \delta(ACo)^{-\lambda t}$ namely assume for small

perturbations a first order rate of re-equilibration. Then, given

$$\frac{d\delta(A)}{dt} = -\lambda \delta(A), \text{ and } d\delta(AC)/dr = -\lambda \delta(AC):$$

$$\left[k_1 + k_{-1} + k_2(C) - \lambda\right]\delta(A) + \left[k_{-1} - k_2(A) - k_{-2}\right]\delta(AC) = 0$$

$$k_2(C)\delta(A) - \left[k_2(A) + k_{-2} - \lambda\right]\delta(AC) = 0$$

The system of two eqs. has solutions if:

$$\begin{vmatrix} \left[k_1 + k_{-1} + k_2(C) - \lambda\right] & \left[k_{-1} - k_2(A) - k_{-2}\right] \\ k_2(C) & -\left[k_2(A) + k_{-2} - \lambda\right] \end{vmatrix} = 0$$

leading to

$$\lambda^2 - S\lambda + P = 0$$

where $S = k_2\{(A)+(C)\} + k_{-2} + k_1 + k_{-1}$

$$P = (k_1 + k_{-1})\left[k_2(A)+k_{-2}\right] + k_2 k_{-1} (C)$$

with solutions

$$\lambda_{I,II} = \tau_{I,II}^{-1} = \tfrac{1}{2}\left[S \pm \sqrt{S^2 - 4P}\right]$$

With the plus and minus sign referring to $\tau_I^{-1}$ and $\tau_{II}^{-1}$ respectively.

For loosely coupled reactions ($k_1$, $k_{-1} >> k_2$, $k_{-2}$) take $S^2 >> 4P$.

Then, the "fast" relaxation time is given by

$$\boxed{\tau_I^{-1} = S \cong k_1 + k_{-1}}$$

and the "slow" relaxation time is given

$$\tau_{II}^{-1} = \frac{P}{S} = \frac{(k_1 + k_{-1})\left[k_2(A)+k_{-2}\right]}{k_1 + k_{-1}} \quad \frac{k_2 k_{-1}}{k_1 + k_{-1}} (C)$$

having expanded $S - S\left(1 - \frac{4P}{S^2}\right)^{1/2} \approx S - S\left(1 - \tfrac{1}{2}\frac{4P}{S^2}\right) = \frac{2P}{S}$ .

Then

$$\tau_{II}^{-1} = k_2(A) + k_{-2} + \frac{k_{-1}}{k_1 + k_{-1}} k_2 (C)$$

$$\boxed{\tau_{II}^{-1} = k_{-2} + k_2 \left[(A) + \frac{k_{-1}}{k_1 + k_{-1}} (C)\right]}$$

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